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## EFFECT OF THE ISOTOPIC COMPOSITION OF LITHIUM CARRIERS ON THE IONIC CONDUCTIVITY OF LANTHANUM LITHIUM TITANATE CERAMIC

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The ionic conductivity of the solid electrolyte  $\text{La}_{2/3-x}\text{Li}_{3x}\text{TiO}_3$  at temperatures 20–600°C with different isotopic composition of the lithium current carriers is measured. It is shown that it has two components — low- and high-temperature — with very different activation energies. NMR on  $^7\text{Li}$  nuclei is used to measure the spin-lattice relaxation rate of the carriers. It is determined that the activation energies of short- and long-range carrier motion are the same at temperatures 20–500°C and are sharply different at higher temperatures. The effect of the concentration of cationic vacancies on the motion of carriers with different isotopic composition is investigated.

In a previous work we investigated the effect of the isotopic composition of lithium current carriers on ion transport in a nitride ceramic, which is solid electrolyte (SEL) and has the average lithium-cation conductivity at temperatures 300–500°C (approximately  $10^{-2} \Omega^{-1} \cdot \text{cm}^{-1}$  at 500°C). We found that the ionic conductivity of such materials depends strongly on the ratio of the  $^7\text{Li}$  and  $^6\text{Li}$  concentrations [1–3].

It is of particular interest to study such dependences for ceramic samples of electrolytes whose conductivity at low temperatures is high. A typical example of such materials is a ceramic based on the solid electrolyte  $\text{La}_{2/3-x}\text{Li}_{3x}\text{TiO}_3$  (LLTO), whose ionic conductivity is about  $10^{-3} \Omega^{-1} \cdot \text{cm}^{-1}$  at 20°C. Such a high conductivity of LLTO is due to a high concentration of cationic vacancies in the layers of the perovskite lattice which are weakly populated by lanthanum ions and which alternate with layers which are densely populated by these particles. The total concentration of the cationic vacancies in the compound can vary over wide limits, since the form in which it is expressed  $\text{La}_{2/3-x}\text{Li}_{3x}\square_{1/3-2x}\text{TiO}_3$ , proposed by some authors [4, 5], shows that it is determined only by the ratio of the lanthanum and lithium concentrations. Here the symbol  $\square$  denotes vacancies in the cationic

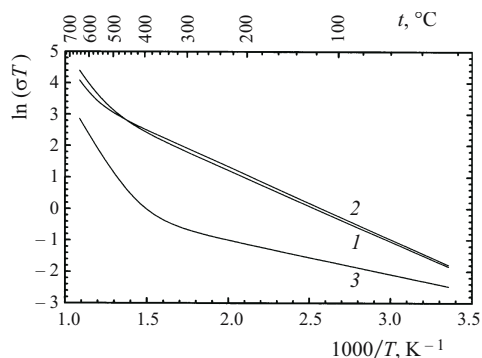
sublattice. In addition, ceramic samples of LLTO compact well, sinter to a dense state, and have high mechanical strength. Our objective in the present work is to investigate the dependence of the isotopic effects on the vacancy concentrations in the lattices of such ceramic materials.

The samples were synthesized by the solid-phase method using the following initial substances: pure-grade  $\text{La}_2\text{O}_3$  and  $\text{TiO}_2$  and lithium-containing concentrated precipitate. The lithium-containing precipitates with prescribed concentrations of the isotopes  $^7\text{Li}$  and  $^6\text{Li}$  were obtained as follows. Metallic lithium with the naturally occurring  $^6\text{Li}$  concentration (7.5%)<sup>2</sup> and  $^6\text{Li}$ -enriched (91.2%) were dissolved in isopropyl alcohol, adding water gradually. Solid residues were filtered out of the solutions and the total lithium content was determined. To obtain a definite isotopic composition in the samples the required volumes of the solutions were mixed and their composition was checked on the “Spectromass 2000” setup with inductively coupled plasma. The solution was evaporated to a gel state and heated for 4–5 h at 400°C after which the total lithium content in the samples was determined again. The computed amounts of lithium-containing mass and lithium and titanium oxides were mixed and ground in an agate mortar. The mixture was briquetted into 7–8 mm in diameter and 4–5 mm thick pellets. The samples were placed into corundum crucibles in a furnace.

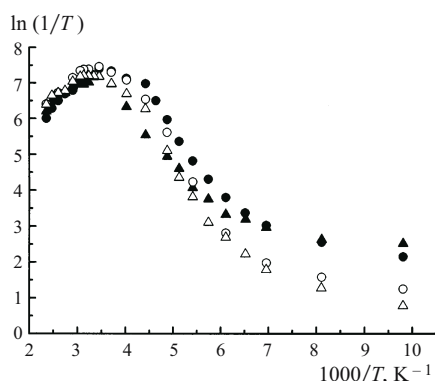
Synthesis was performed in four stages. The materials were ground between stages. At the first stage the tempera-

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<sup>2</sup> Here and below, unless otherwise stated, the atomic content.



**Fig. 1.** Temperature dependences of the volume conductivity of LLTO with  $C_{\square} = 5\%$  and different  ${}^6\text{Li}$  content: 7.50% (1), 48.64% (2), and 91.2% (3).



**Fig. 2.** Characteristic temperature dependences of the spin-lattice relaxation rates ( $1/T$ ,  $\text{sec}^{-1}$ ) of  ${}^7\text{Li}$  nuclei in a LLTO lattice ( $C_{\square} = 5\%$ ): (●) 7.50%  ${}^6\text{Li}$ , 13 MHz; (○) 7.50%  ${}^6\text{Li}$ , 35 MHz; (▲) 74.54%  ${}^6\text{Li}$ , 13 MHz; (△) 74.54%  ${}^6\text{Li}$ , 35 MHz.

ture was maintained at 900°C for 10 h. At the next three stages the synthesis temperature was 1200°C and the soaking time was also 10 h. The completeness of synthesis was monitored by the x-ray method using  $\text{CuK}_{\alpha}$  radiation in a DRON-3.5M diffractometer. All lines of the perovskite structure, including the lines due to the superstructure along the  $c$  axis, are present in the x-ray diffraction patterns. It should be noted that in the x-ray diffraction patterns the impurity lines of the product of the interaction of the initial mass with the corundum crucible do not exceed the background level and are visible only in the neutron diffraction patterns obtained with high exposure. They show that the quantities of the product ( $\gamma\text{-LiAlO}_2$ ) of the interaction of the samples with the crucible are small.

The porosity of the samples was 5–15 vol.%. All results obtained were adjusted to dense material using the relation presented in [6].

In connection with the report that the material is prone to quenching as a result of the high concentration of defects [4, 5, 7], we paid special attention to the conditions under which the samples were cooled at the final stage of synthesis.

The samples were slowly cooled (no faster than 1 K/min to maintain an equilibrium vacancy distribution in the volume of the crystal lattice) to 600°C and removed from the furnace to deposit the electrodes. A paste containing silver was deposited on the end face of a hot sample, heated at 600°C until organic residues were removed, and cooled to room temperature at the previous rate.

The measurements (using ac current) of the electric conductivity of the solid electrolyte  $\text{La}_{2/3-x}\text{Li}_{3x}\text{TiO}_3$  with different concentrations of lithium isotopes and vacancies were performed at temperatures ranging from room temperature to 600°C in  $\text{Ag}, \text{O}_2 \mid \text{LLTO} \mid \text{O}_2, \text{Ag}$  cells in air. The working frequency of the measurements was 10 kHz. The measurements were performed with an E7-14 imittance meter with heating and cooling of the cells. The characteristic temperature dependences of the volume conductivity of the ceramic samples of the electrolyte LLTO with different concentrations of lithium isotopes are presented in Fig. 1 in Arrhenius coordinates. The data were used as a basis for calculating the activation energy of conduction with respect to lithium ions, which are well-known [7] to characterize the long-range carrier motion (in the literature the long-range motion with respect to ionic transport is taken to mean the displacements of current carriers over a distance of the order of several unit cells).

To obtain information on the short-range motion of lithium carriers, i.e., on hopping over the interatomic distance in the electrolyte lattice, the spin-lattice relaxation rates of the  ${}^7\text{Li}$  nuclei were measured for different  ${}^6\text{Li}$  concentrations by the NMR method. The working frequencies of the measurements were 13 and 35 MHz. The characteristic temperature dependences of the spin-lattice relaxation rates, close at all frequencies, are presented in Fig. 2. The activation energies of the short-range carrier motion were calculated from the temperature dependences of the spin-lattice relaxation rates (Fig. 3).

The activation energies of short- and long-range motion,  $U$  and  $E$ , respectively, are presented in Tables 1 and 2.

It follows from Fig. 1 that the lithium ion conductivity of the solid electrolyte LLTO consists of low- and high-temperature components. The low-temperature component is high up to 450°C with low values of the activation energy characteristic of superionic conductors. Moreover, the activation energies for short- and long-range carrier motion are equal to one another at these temperatures. The results attest to the absence of strong correlations between lithium carrier hops up to 450°C. This can be explained by tying the low-temperature conductivity to the existence of highly conducting cationic layers  $[0\ 0\ 0]$ , containing predominately vacancies and lithium cations, in the electrolyte lattice [4, 5]. According to the data obtained in these works, at room temperature up to 80% of the lanthanum cations are concentrated in other layers  $[0\ 0\ 1/2]$ , where the conductivity is low.

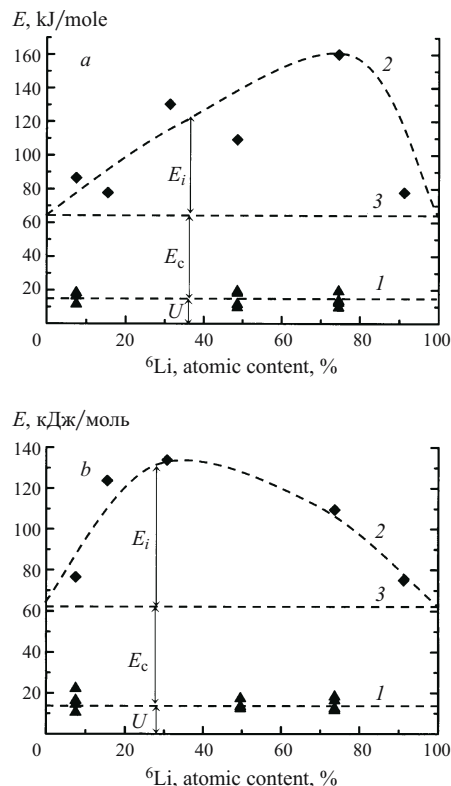
Thus, layers of the first type determine the electric conductivity of the samples at low temperatures. Apparently, the

optimal ratio of the concentrations of lithium and cation vacancies is created in these layers, resulting in a loss of correlations between carrier hops and carrier motion in the form of independent particles which overcome only the true barriers formed during the formation of the crystal. Such a situation leads to a superionic state of the crystal, which is possible in structures with high concentrations of defects or in "open" lattices with large free volumes.

As temperature increases, the lanthanum cations become distributed over the layers more uniformly, which likewise gives rise to a more uniform distribution of the lithium ions and cationic vacancies over the crystal. Lanthanum transitions result in vanishing of the superconducting layers and in an increase of the activation energy of the conduction starting at 400–500°C (see Fig. 1). Its values become 3–4 times greater than the true energy barrier and start to depend on the ratio of the concentrations of the isotopes of the lithium carriers. Such facts attest too the appearance of strong correlation phenomena in the system of carriers. Two distinct types of correlations appear: coulomb and ionic. The correlation effects are clearly seen in Fig. 2.

The data in Fig. 3 make it possible to distinguish the contributions of both types of correlations as follows. Extrapolating the curves 1 and 2 to zero concentrations of the isotopes  $^6\text{Li}$  and  $^7\text{Li}$ , we obtain on the ordinate the values of the activation energies for short- and long-range motions in a "monoisotopic" electrolyte. The difference of these quantities is approximately 50 kJ/mole. Evidently, it can be interpreted as the coulomb correlation energy. The magnitude of this type of correlation is independent of the isotopic composition, since the total concentration of the lithium carriers in the electrolyte remains unchanged. The changed values of the remaining part of the energy of long-range motion must be ascribed to isotopic correlation, whose maximum energy in LLTO reaches 100 kJ/mole with  $C_{\square} = 5\%$  and 70 kJ/mole with  $C_{\square} = 10\%$ .

It is our opinion that such a strong isotopic correlation, resulting in a substantial decrease of the number of hops of mobile carriers, is due to the fact that carrier–vacancy ex-



**Fig. 3.** Activation energy of short-range ( $\blacktriangle$ ) and high-temperature long-range ( $\blacklozenge$ ) motion of lithium carriers in  $\text{La}_{2/3-x}\text{Li}_{3/3-x}\text{TiO}_3$ : a)  $C_{\square} = 5\%$ ; b)  $C_{\square} = 10\%$ ; U) activation energy of short-range motion;  $E_c$ ) Coulomb correlation energy;  $E_i$ ) isotopic correlation energy; 1) U; 2) sum of U,  $E_c$ , and  $E_i$ ; 3) sum of U and  $E_c$ .

change is forbidden at the moment when an isotope of the second type occupies the vacancy. When monoisotopic carriers are diluted by particles with a different mass, their hops are no longer coordinated because of the difference in the frequency of the oscillations. Particles of different type start to interfere with each other's motion, which results in a higher effective activation energy. This effect is especially strong when a vacancy deficit appears with vanishing of the superconducting layers in the electrolyte lattice.

**TABLE 1.**

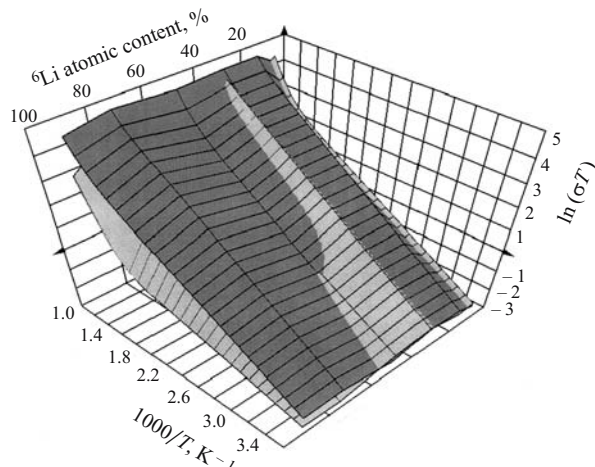
$^6\text{Li}, \%$ *	$C_{\square}, \%$ *	Short-range motion activation energy, kJ/mole			
		13 MHz		35 MHz	
		low-temperature	high-temperature	low-temperature	high-temperature
7.50	5	16.40	11.58	18.33	11.58
48.64		18.33	9.65	19.30	11.58
74.54		12.54	13.51	19.30	9.65
7.50	10	22.19	10.61	14.47	16.40
49.62		13.51	12.54	17.37	13.51
73.68		18.33	12.54	16.40	11.58

\* Atomic content.

**TABLE 2.**

$^6\text{Li}, \%$ *	$C_{\square}, \%$ *	Long-range motion activation energy, kJ/mole	
		low-temperature	high-temperature
7.50	5	18.75	86.55
48.64		19.15	109.35
74.54		21.00	160.18
7.50	10	18.75	86.55
49.62		19.15	109.35
73.68		21.00	160.18

\* Atomic content.



**Fig. 4.** Volume conductivity ( $\sigma T$ ,  $\text{S} \cdot \text{cm}^{-1} \cdot \text{K}^{-1}$ ) of the electrolyte versus the atomic content of the isotopes  $^6\text{Li}$  and the reciprocal of the temperature: (□) LLTO with  $C_{\square} = 5\%$ ; (■) LLTO with  $C_{\square} = 10\%$ .

The effect of the total concentration of vacancies on the correlation phenomena in the solid superconductor LLTO is of particular interest. It is evident from Tables 1 and 2 that intercarrier correlation phenomena in the electrolyte become weaker as the concentration of vacancies along which ion transport occurs increases.

Figure 4 shows the results obtained for the conductivity  $\sigma$  of the compound LLTO at different vacancy concentrations. It is evident that the electric conductivity depends on the isotopic composition of the carriers, especially at high temperatures and concentration of vacancies in the cationic sublattice, and it increases as their fraction increases.

In summary, the volume conductivity at low temperatures, when superconducting cationic layers exist, depends weakly on the isotopic composition of the lithium carriers, and the activation energy of short-range motion equals that of long-range motion.

At elevated temperatures the superconducting layers vanish as a result of the redistribution of defects and two

types of strong intercarrier correlation effects appear — coulomb and isotopic. The correlations of the first type are due to a high concentration of charged carriers and those of the second type are due to the mutual influence of the isotopes during isotope ion – vacancy exchange.

An increase of the concentration of vacancies in  $\text{La}_{2/3-x}\text{Li}_{3x}\text{TiO}_3$ , along which ion transfer occurs, results at temperatures 20 – 500°C in weaker correlations between carrier hops and, ultimately, in the appearance of layers with superionic conductivity. At higher temperatures the superionic state vanishes as a result of particle mixing along the lattice layers and averaging of their concentrations.

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